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of Aqueous Nickel Chloride at 25°C

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This paper was prepared for submittal to  
Journal of Chemical and Engineering Data

June, 1985

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Y9600 R011A1-1001  
JAC 11 27 1981  
24250 1001

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Densities and Apparent Molal Volumes of Aqueous  
Nickel Chloride at 25°C

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Abstract

Densities of aqueous  $\text{NiCl}_2$  solutions were measured from 0.04 to 4.98 mol (kg  $\text{H}_2\text{O}$ )<sup>-1</sup> at 25.00°C using very high purity  $\text{NiCl}_2$ . Each density was measured in duplicate using 31-cm<sup>3</sup> single-stem pycnometers. These experimental densities are critically compared to published literature data, and least-squares equations were used to represent the higher quality data.

## Introduction

Density data for aqueous electrolyte solutions are required for a number of applications including conversion of mass concentration to volumetric concentrations, for making buoyancy corrections when weighing samples, for converting mean molal activity coefficients to mean molar values, and for calculation of partial molal volumes. These partial molal volumes are related to the pressure derivatives of solute and solvent chemical potentials (1). In addition, volumetric data provide information about ion-solvent and ion-ion interactions.

We have been characterizing various aqueous electrolytes at 25.00°C in terms of their osmotic and activity coefficients, their mutual diffusion coefficients, and their densities and apparent molal volumes. We have reported such data for alkali metal and alkaline earth metal chlorides (2-5), and have recently extended these measurements to include the transition metal chlorides  $\text{MnCl}_2$ ,  $\text{CdCl}_2$ , and  $\text{ZnCl}_2$  (6-9). We investigated  $\text{MnCl}_2$  because it appears to be a fairly strong electrolyte,  $\text{CdCl}_2$  because it is a highly self-complexed electrolyte, and  $\text{ZnCl}_2$  because it is intermediate in behavior.

Of the transition metal aquo ions,  $\text{Ni}^{2+}$  is the most extensively studied by spectroscopic and diffraction methods. There is nearly universal agreement that  $\text{Ni}(\text{H}_2\text{O})_6^{2+}$  is the dominant species in aqueous solutions of  $\text{NiCl}_2$  and  $\text{Ni}(\text{ClO}_4)_2$  (10). However, Weingärtner et al. (11) summarized various types of evidence that one mol  $(\text{kg H}_2\text{O})^{-1}$   $\text{NiCl}_2$

solutions contain 5-15% inner-sphere monochloro complex. Thermodynamic and transport data for  $\text{NiCl}_2$  solutions are therefore important, since it is one of the few electrolytes whose aqueous solution coordination is fairly well understood.

Density data for aqueous  $\text{NiCl}_2$  solutions at  $25^\circ\text{C}$  have been reported by a number of workers (12-17). The results of Karapet'yants et al. (12) are seriously discrepant from all the other studies, up to 3% high at  $4.08 \text{ mol (kg H}_2\text{O)}^{-1}$ , and can be rejected as highly inaccurate. The other data (13-17) agree with each other much better, but still show differences several times greater than expected from the usual stock solution concentration errors. We, therefore, reinvestigated  $\text{NiCl}_2$  densities from 0.04 to  $4.98 \text{ mol (kg H}_2\text{O)}^{-1}$  and report these results here. We are also remeasuring osmotic/activity coefficients (18) and diffusion coefficients (19) for aqueous  $\text{NiCl}_2$ .

### Experimental Section

All of our  $\text{NiCl}_2$  densities were measured in duplicate at  $25.00 \pm 0.005^\circ\text{C}$  (IPTS-68) using two matched  $30.87 \text{ cm}^3$  single-stem pycnometers. These pycnometers were wiped with 95% ethanol about 0.5 h before weighing. All weights were corrected to vacuum.  $\text{NiCl}_2$  solution densities are uncertain by  $2-3 \times 10^{-5} \text{ g cm}^{-3}$ .

Pycnometer volumes are known to  $3-4 \times 10^{-4} \text{ cm}^3$ , and were obtained by calibration 7-9 times using purified water. Our water was purified first by

ion-exchange and then by distillation. The density of water at 25.00°C, 0.997045 g cm<sup>-3</sup>, was taken from Kell (20).

Our aqueous NiCl<sub>2</sub> stock solution was prepared by dissolving and filtering Mallinckrodt analytical reagent NiCl<sub>2</sub>·6H<sub>2</sub>O. Lower concentrations were obtained by mass dilution; higher concentrations were obtained by gently warming samples to drive off water.

Direct current arc optical emission spectroscopic analysis of this NiCl<sub>2</sub>·6H<sub>2</sub>O for impurities indicated the presence of 10 ppm Sr, ≤ 5 ppm Si, and ≤ 1 ppm Ca by weight. The anticipated main impurity, Co, was actually below its 10 ppm detection limit.

We have analyzed the concentrations of several other transition metal chloride solutions both by mass titration with AgNO<sub>3</sub> (dichlorofluorescein end-point indicator), and by conversion to the anhydrous sulfate by addition of excess H<sub>2</sub>SO<sub>4</sub> followed by evaporation and drying at 400-500°C (6-9). However, the green color of NiCl<sub>2</sub> solutions makes it rather difficult to detect the yellow to pink dichlorofluorescein end-point color change. An attempt to convert samples of NiCl<sub>2</sub> to anhydrous NiSO<sub>4</sub> at 500°C gave results that were initially about 1.5% high, but which became low after a few days and showed a steady weight decrease with time. This apparently indicates that partial formation of Ni polysulfate occurs initially, and that this Ni sulfate/polysulfate is thermodynamically unstable in air at 500°C and gradually decomposes to NiO. Thus, neither of these methods is satisfactory for quantitative analysis.

We then attempted to obtain the stock solution concentration by dehydration of acidified samples in air at 200°C. The "NiCl<sub>2</sub>" sample changed color with time from orange-yellow to brownish yellow, and sample weights decreased with time. Clearly the NiCl<sub>2</sub> was being slowly converted to NiO. At higher temperatures most of the material was converted to NiO, but some chloride still seemed to remain so this method is unsatisfactory. An additional attempt to get NiO by precipitation of NiCl<sub>2</sub> with aqueous ammonia followed by thermal decomposition had similar problems. Ni<sub>2</sub>O<sub>3</sub>·nH<sub>2</sub>O formation was not a problem since it decomposes to NiO at 400°C (21).

The method finally chosen for concentration analysis is as follows. Weighed NiCl<sub>2</sub> stock solution samples were evaporated to dryness with excess H<sub>2</sub>SO<sub>4</sub>; this eliminates the chloride ions and gives bright yellow Ni sulfate/polysulfate. This was then decomposed in air to form NiO at 800°C. After about 5 days at 800°C the decomposition was complete, and sample weights were constant after that. The NiO was greenish-gray ash colored.

The NiCl<sub>2</sub> stock solution concentration was thus determined to be  $3.9221 \pm 0.0012 \text{ mol (kg H}_2\text{O)}^{-1}$  using triplicate samples. Assumed molecular masses are 129.616 g mol<sup>-1</sup> for NiCl<sub>2</sub> and 74.709 g mol<sup>-1</sup> for NiO.

X-ray fluorescence spectroscopic analysis of NiO prepared in this manner showed it contained <0.015% Cl and <0.02% S. These impurity amounts are too low to affect the calculated stock concentration, so thermal decomposition of Ni sulfate/polysulfate to NiO is suitable for quantitative analysis for Ni.

## Results and Discussion

Table I contains the experimental density data for aqueous  $\text{NiCl}_2$  at  $25^\circ\text{C}$ . Although the highest concentration of  $4.9832 \text{ mol (kg H}_2\text{O)}^{-1}$  is slightly above the solubility (18) of  $4.9208 \pm 0.0028 \text{ mol (kg H}_2\text{O)}^{-1}$ , no crystallization occurred during the density measurements. Quantities tabulated in Table I are the molality  $m$  in  $\text{mol (kg H}_2\text{O)}^{-1}$ ; the molarity  $c$  in  $\text{mol dm}^{-3}$ ; the density  $d$  in  $\text{g cm}^{-3}$ ; and the apparent molal volume  $\phi_v$  of  $\text{NiCl}_2$  in  $\text{cm}^3 \text{ mol}^{-1}$ . These apparent molal volumes were calculated by using the equation

$$\phi_v = \frac{10^3(d^\circ - d)}{m d^\circ} + \frac{M_2}{d} \quad (1)$$

where  $M_2$  is the molecular weight of  $\text{NiCl}_2$  and  $d^\circ = 0.997045 \text{ g cm}^{-3}$  is the density of pure water.

These density data were represented by the least-squares equations

$$d = d^\circ + \sum_{i=2}^n B_i X^{i/2} \quad (2)$$

where  $X$  denotes  $m$  or  $c$ . Table II contains the least-squares values of  $B_i$  and the standard deviations  $\sigma$  of eq. 2. The values of  $\sigma$  were  $1.1 \times 10^{-5} \text{ g cm}^{-3}$  (maximum deviation of  $2.1 \times 10^{-5} \text{ g cm}^{-3}$ ) for the molarity fit and  $\sigma = 1.4 \times 10^{-5} \text{ g cm}^{-3}$  (maximum deviation  $2.8 \times 10^{-5} \text{ g cm}^{-3}$ ) for the molality fit; they are well within our claimed accuracy of  $2\text{--}3 \times 10^{-5} \text{ g cm}^{-3}$ .



Published density data for  $\text{NiCl}_2$  solutions cover the concentration ranges 0.0200-4.081 (12), 0.0999-4.9111 (13), 0.04488-0.2015 (14), 0.00366-4.210 (15), 0.04099-0.91782 (16), and 0.09554-5.384 mol (kg  $\text{H}_2\text{O}$ )<sup>-1</sup> (17). The data of Karapet'yants et al. (12) are considerably higher than all of the other studies so they were rejected. Pearce and Eckstrom's values (13) are somewhat low, up to  $4-5 \times 10^{-4} \text{ g cm}^{-3}$  at high concentrations. This set of data (13) was also rejected, even though it is low only by about the same amount that the better quality data sets differ. The reason it was rejected was because their densities (13) show a significantly different variation with concentration than the three other high concentration data sets (this work and references 15 and 17). Also, the points of Stokes et al. (15) at 0.08280, 0.10403, and 0.11670 mol (kg  $\text{H}_2\text{O}$ )<sup>-1</sup> are inconsistent with their own data at other concentrations, so these three points were also rejected.

The least-squares parameters for eq. 2 were then redetermined by giving equal weight to our data and to the more reliable published data (14-17). Table II contains these new  $B_i$  values, and Figure 1 shows the differences between the experimental data and the least-squares equations for both molality and molarity fits.

Our density data agree best with that of Stokes et al. (15), but their results are slightly lower. The data of Lo Surdo and Millero (16) agree with ours up to 0.16 mol (kg  $\text{H}_2\text{O}$ )<sup>-1</sup>, but theirs are higher than ours at higher concentrations. Perron et al. (17) agree with our densities up to about 0.5 mol (kg  $\text{H}_2\text{O}$ )<sup>-1</sup>, but their data are intermediate between us and Lo Surdo and Millero (16) at higher concentrations. Data from Spitzer et al. (14) tend

to be slightly low. It should be noted that our data fall between results from the other two studies (15,17) that were based on use of high purity  $\text{NiCl}_2$ .

### Acknowledgment

We thank John G. Albright for the loan of his pycnometers, Sue Frument for typing the manuscript, and John G. Albright and Donald G. Miller for assistance with calculations. This work was performed under the auspices of the U. S. Department of Energy by Lawrence Livermore National Laboratory under contract number W-7405-ENG-48.

### Glossary

- d     density of solution in  $\text{g cm}^{-3}$
- $d^\circ$    density of pure water in  $\text{g cm}^{-3}$
- m     molal concentration of solute in  $\text{mol (kg H}_2\text{O)}^{-1}$
- c     molar concentration of solute in  $\text{mol dm}^{-3}$
- $\phi_v$    apparent molal volume of solute in  $\text{cm}^3 \text{mol}^{-1}$
- $M_2$    molecular weight of solute in  $\text{g mol}^{-1}$
- $B_i$    least-squares coefficients for eq. 2
- X     denotes m or c in eq. 2
- $\sigma$      standard deviation of eq. 2

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Table I. Densities and Apparent Molal Volumes of Aqueous  $\text{NiCl}_2$  at  $25.00^\circ\text{C}$ 

$m, \text{mol (kg H}_2\text{O)}^{-1}$	$c, \text{mol dm}^{-3}$	$d, \text{g cm}^{-3}$	$\phi_v, \text{cm}^3 \text{mol}^{-1}$
0.039987	0.039856	1.001893	8.00
0.089987	0.089654	1.007912	8.43
0.15996	0.15926	1.016247	9.07
0.24988	0.24853	1.026805	9.90
0.35986	0.35745	1.03966	10.43
0.48997	0.48590	1.05466	11.07
0.64587	0.63914	1.07242	11.72
0.81012	0.79975	1.09087	12.34
0.99961	0.98393	1.11184	12.99
1.2097	1.1866	1.13471	13.64
1.4398	1.4066	1.15930	14.31
1.6661	1.6209	1.18301	14.93
1.9994	1.9329	1.21728	15.72
2.0001	1.9336	1.21734	15.73
2.3331	2.2404	1.25067	16.46
2.6652	2.5418	1.28314	17.11
3.0008	2.8414	1.31519	17.70
3.3082	3.1117	1.34393	18.19
3.6128	3.3756	1.37187	18.63
3.9221	3.6394	1.39964	19.05
4.2549	3.9187	1.42890	19.47
4.4271	4.0613	1.44380	19.67
4.9832	4.5133	1.49071	20.30

Table II. Coefficients for  $\text{NiCl}_2$  Density Polynomials

$B_i$	Molarity <sup>a</sup>	Molality <sup>a</sup>	Molarity <sup>b</sup>	Molality <sup>b</sup>
$B_2$	0.123963	0.123283	0.121639	0.122701
$B_3$	-0.0120816	-0.0105978	-0.00203718	-0.00671096
$B_4$	0.0122930	0.00894802	-0.00399048	0.000614096
$B_5$	-0.0117619	-0.0103255	0.00106881	-0.00231334
$B_6$	0.00496078	0.00411775		0.000573561
$B_7$	-0.000755002	-0.000587033		
Maximum Concentration	4.5133	4.9832	4.8382	5.384
$\sigma$	0.000011	0.000014	0.000170	0.000236

<sup>a</sup>Data from Table I only.<sup>b</sup>Data from Table I and references 14-17.

### Figure Caption

Fig. 1 Differences between experimental densities and least-squares equations for  $\text{NiCl}_2$  solutions in  $\text{g cm}^{-3} \times 10^5$ : (●) this research; (x) Spitzer et al. (14); (◇) Stokes et al. (15); (Δ) Lo Surdo and Millero (16); (o) Perron et al. (17). Top curve is for molarity fit; bottom curve is for molality fit.



